

AD-A250 215



2

Office of Naval Research

Grant: N00014-91-J-1625

R&T Code: 4132051-01

Technical Report No. 9

**Organic Main-Chain NLO Polymers. 1. Copolymerization
of Bis(arylcarboxaldehyde) and Bis(cyanoacetate)
Monomers Via the Knoevenagel Condensation.**

by

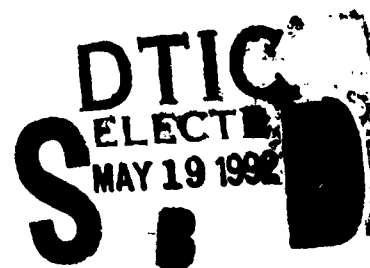
Michael E. Wright & Sanjoy Mullick

*Department of Chemistry & Biochemistry, Utah State University,
Logan, Utah 84322-0300*

Accepted for Publication in

Macromolecules

May 10, 1992



Reproduction in whole, or in part, is permitted for any purpose of the United States Government.

This document has been approved for public release and sale; its distribution is unlimited.

92 5 18 076

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
<small>Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.</small>				
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE May 10, 1992	3. REPORT TYPE AND DATES COVERED 15 April, 1991 - 15 April, 1992		
4. TITLE AND SUBTITLE Organic Main Chain NLO Polymers. 1. Copolymerization of Bis(arylcarboxaldehydes) and Bis(cyanoacetate) Monomers		5. FUNDING NUMBERS N00014-91-J1625		
6. AUTHOR(S) Michael E. Wright & Sanjoy Mullick				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Utah State University Department of Chemistry & Biochemistry Logan, UT 84322-0300		8. PERFORMING ORGANIZATION REPORT NUMBER Technical Report #9		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Department of the Navy Office of Naval Research 800 North Quincy Street Arlington, VA 22217-5000		10. SPONSORING/MONITORING AGENCY REPORT NUMBER 4132051		
11. SUPPLEMENTARY NOTES Macromolecules, in press.				
12a. DISTRIBUTION / AVAILABILITY STATEMENT Reproduction in whole or in part is permitted for any purpose of the United States Government. This document has been approved for public release and sale; its distribution is unlimited.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Two monomers, 4-[CO ₂ Et(CN)C=CH]C ₆ H ₄ O(CH ₂) ₆ OH (2) and 4-(CHO)C ₆ H ₄ O-(CH ₂) ₆ O ₂ CCH ₂ CN (3), both containing NLO-phores, were prepared and polymerized by different methods. The Knoevenagel polycondensation technique provided polymers of good molecular weight and tractable in organic solvents. A series of bis(carboxaldehyde) comonomers were prepared in the study, [4-(CHO)C ₆ H ₄] ₂ R {4a, R= (CH ₂) ₄ ; 4b, R= (CH ₂) ₅ ; 4c, R= (CH ₂) ₆ ; 4d, R= 1,2-(CH ₂) ₂ C ₆ H ₄ }, and copolymerized with CNCH ₂ CO ₂ (CH ₂) ₆ O ₂ CCH ₂ CN to afford new series of accordion polymers (6) which contain NLO-phores. The copolymers were obtained with molecular weights (M _n) in the range of 3100 to 30,100 and λ _{max} of ~346 nm. We did not observe T _g 's for the copolymers above 10 °C, only T _m 's in the range of 123 to 200 °C.				
14. SUBJECT TERMS Nonlinear Optical; Polymers; Knoevenagel condensation; Accordion polymers; Main-Chain NLO Polymers			15. NUMBER OF PAGES 22 pages	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL	

**Organic Main-Chain NLO Polymers. 1. Copolymerization of
Bis(arylcarboxaldehydes) and Bis(cyanoacetate)
Monomers Via the Knoevenagel Condensation.**

Michael E. Wright* and Sanjoy Mullick

*Department of Chemistry & Biochemistry, Utah State University,
Logan, Utah 84322-0300*

Abstract. Two monomers, 4-[CO₂Et(CN)C=CH]C₆H₄O(CH₂)₆OH (2) and 4-(CHO)C₆H₄O(CH₂)₆O₂CCH₂CN (3), both containing NLO-phores, were prepared and polymerized by different methods. Monomer 2 was polymerized under transesterification conditions [Ti(OC₄H₉)₄, 150 °C] and 3 through a Knoevenagel polycondensation [4-(dimethylamino)pyridine (DMAP), THF, ~23 °C]. The Knoevenagel polycondensation technique provided polymers of good molecular weight and tractable in organic solvents. A series of *bis*(carboxaldehyde) comonomers were prepared in the study, [4-(CHO)C₆H₄]₂R (4a, R= (CH₂)₄; 4b, R= (CH₂)₅; 4c, R= (CH₂)₆; 4d, R= 1,2-(CH₂)₂C₆H₄), and copolymerized with CNCH₂CO₂(CH₂)₆O₂CCH₂CN to afford new series of accordion polymers (6) which contain NLO-phores. In the case of polymers 6a and 6c we found insolubility limited our ability to characterize the materials. Copolymerization of 4a and 4c with CNCH₂CO₂(CH₂)₈O₂CCH₂CN afforded copolymers 7a and 7c, respectively, which did exhibit good solubility (~10 % by weight) in most organic solvents. The copolymers were obtained with molecular weights (M_n) in the range of 3100 to 30,100 and λ_{max} of ~346 nm. We did not observe T_g's for the copolymers using DSC analysis, only T_m's in the range of 123 to 200 °C.

[End of Abstract]

92-13248

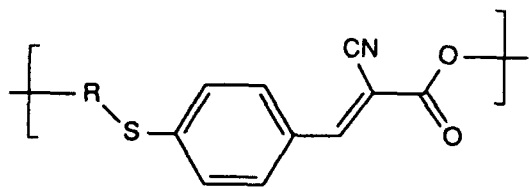


92 5 18 076

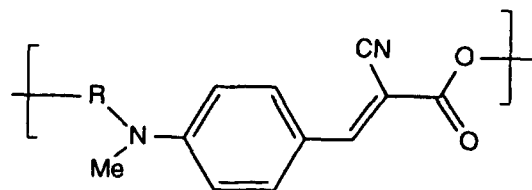
Introduction

The design and synthesis of new NLO materials for SHG applications can be accomplished through a variety of strategies.¹ Polymeric NLO materials are said by many workers in the field to have several design advantages.² The area of polymeric NLO materials within itself possesses numerous design strategies. The NLO-phore can be incorporated as side-chain³ or incorporated into a heavily cross-linked polymer matrix.⁴

A very attractive approach to polymeric NLO materials is the incorporation of the NLO-phore directly in the polymer backbone. Hall and coworkers⁵ prepared the first NLO polymer of this type and shortly thereafter Lindsay and coworkers prepared related NLO main chain polymers (see below).⁶ Although the second harmonic generation (SHG) measurements for the materials prepared by Lindsay and coworkers were not spectacular, they showed a great deal of promise for the main chain NLO-phore in that the materials retained alignment and activity for long periods of time. Theory indicates that if alignment of polymer chains containing a series of repeating units can be achieved there will be a significant enhancement in the NLO properties.

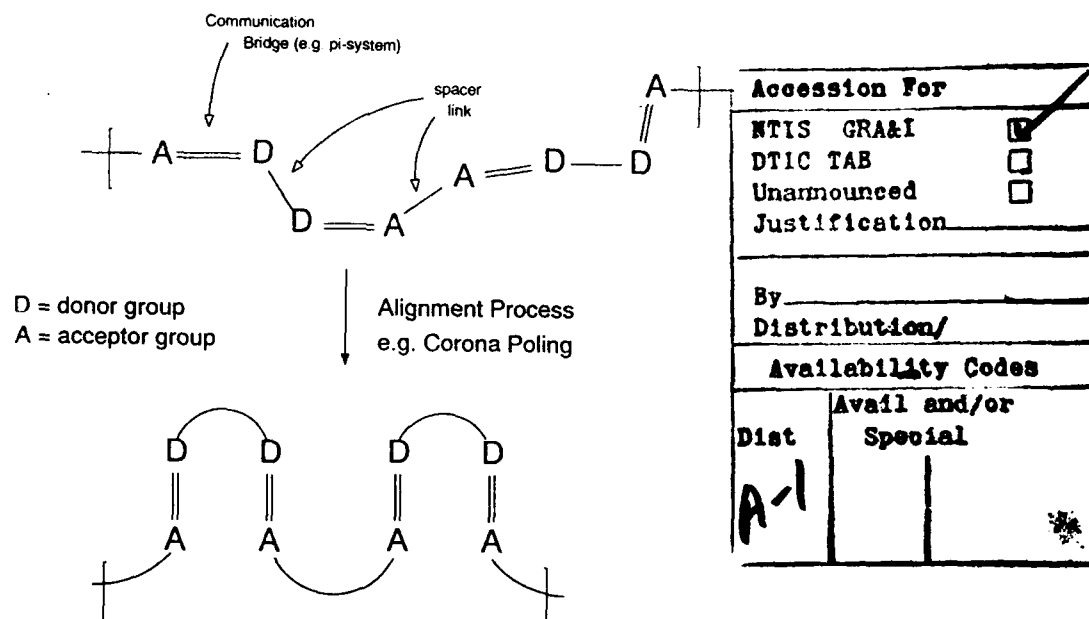


University of Arizona, Hall & coworkers



NWC Chemistry Division, Lindsay & coworkers

A variation to the main chain NLO-phore approach was recently reported by Lindsay and coworkers.^{6b} In this strategy the polymer backbone is folded into an accordion shape with the donor and acceptor groups fixed at alternating apex of the accordion (see below). In the alignment process (*i.e.* corona poling) the need for complete reorientation of a polymer chain is eliminated. In the design of polymeric NLO materials the key to success lies in obtaining materials with a high degree of alignment and the ability to retain that oriented state over long periods of time.



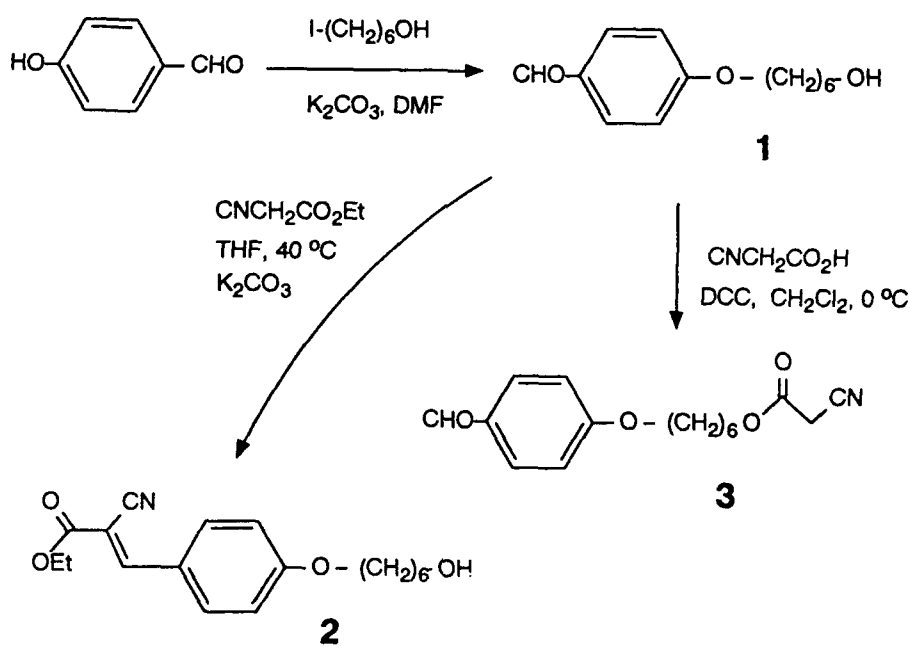
In our efforts to synthesize organometallic NLO polymers we discovered that we could prepare linear and accordion main-chain organometallic NLO polymers⁷ by employing the very mild and efficient Knoevenagel reaction⁸ as a polycondensation technique. In this paper we present our results on the use of the Knoevenagel polycondensation technique for the synthesis of polymers containing organic NLO-phores. The approach is useful for the preparation of both linear and accordion main chain NLO polymers.



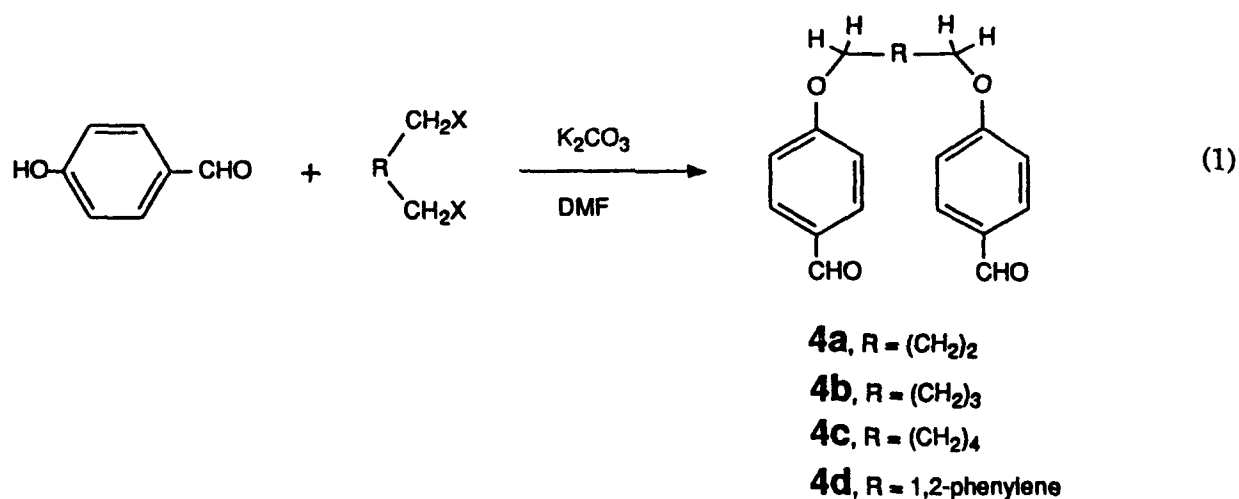
Results & Discussion

Monomer Synthesis. Treatment of *p*-hydroxybenzaldehyde with 6-iodohexanol in the presence of potassium carbonate afforded compound **1** in excellent yield.⁹ The condensation of **1** with ethyl cyanoacetate was carried out employing K_2CO_3 in THF solution. Using a procedure related to that reported by Hall and coworkers^{5d} monomer **2** is prepared using 4-(dimethylamino)pyridine (DMAP) as the base in the Knoevenagel condensation (Scheme 1). Compound **1** was reacted with cyanoacetic acid and the coupling reagent, dicyclohexylcarbodiimide (DCC), to afford in very high yield monomer **3** (Scheme 1).¹⁰ The dicyclohexylurea produced in the synthesis of **3** is removed by filtration and then flash column chromatography on silica gel. Compound **3** is recrystallized from chloroform and hexanes to afford analytical pure monomer. In the pure state monomer **3** is found to be stable indefinitely when stored at $-25\text{ }^\circ\text{C}$.

Scheme 1



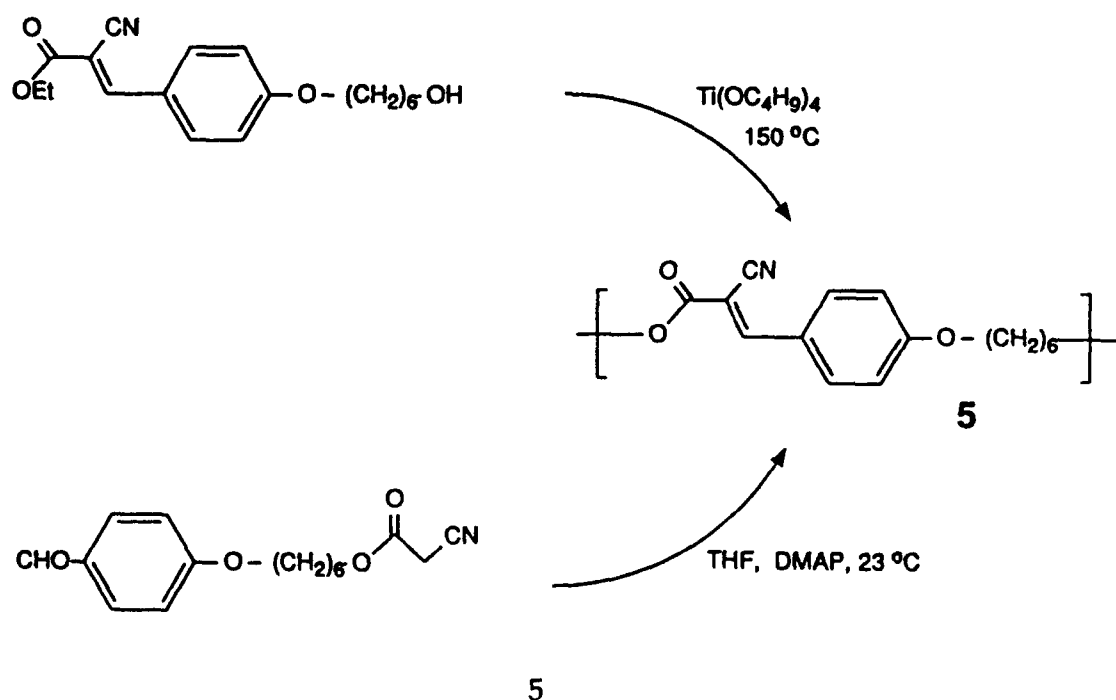
The *bis*(carboxaldehyde) comonomers, **4a-d**, were prepared treatment of the α,ω -diiodoalkanes and 1,2-*bis*(chloromethyl)benzene with *p*-hydroxybenzaldehyde and potassium carbonate in DMF (eq 1). In each case the comonomers were isolated as light yellow or pink microcrystalline solids. Although some of these *bis*(carboxaldehyde) comonomers have been prepared previously,¹¹ we find the use of potassium carbonate in DMF a safe alternative to sodium hydride, sodium metal, or alcoholic potassium hydroxide. Dalton and coworkers have recently reported the synthesis of **4b** using K_2CO_3 /THF/KI and 1,5-dibromopentane with comparable success.¹²



Polymer Synthesis and Characterization. Polymerization of monomers **2** and **3** were carried out employing standard transesterification and Knoevenagel reaction

conditions, respectively (Scheme 2). Since both polymerization reactions yield the same polymer, **5**, it is viewed as an opportunity to contrast the two techniques. The transesterification polycondensation of monomer **2** afforded somewhat lower molecular weight polymer than the Knoevenagel polycondensation (Table 1). Similar results are obtained when using $(\text{Bu})_2\text{Sn}(\text{lutarate})_2$ as the Lewis acid catalyst. However, we did not exhaustively try and optimize the transesterification polymerization conditions so it may be possible to obtain higher molecular weight polymer. The conditions we employed were very similar to those used by both the groups of Hall and Lindsay. The highest average molecular weights ($M_n = \sim 60,000$) are obtained by Hall and coworkers when a comonomer (*e.g.* methyl 12-hydroxydodecanoate) is utilized.^{5d} Our results illustrate that fairly high molecular weight homopolymer can be obtained and exhibit good solubility in common organic solvents.

Scheme 2



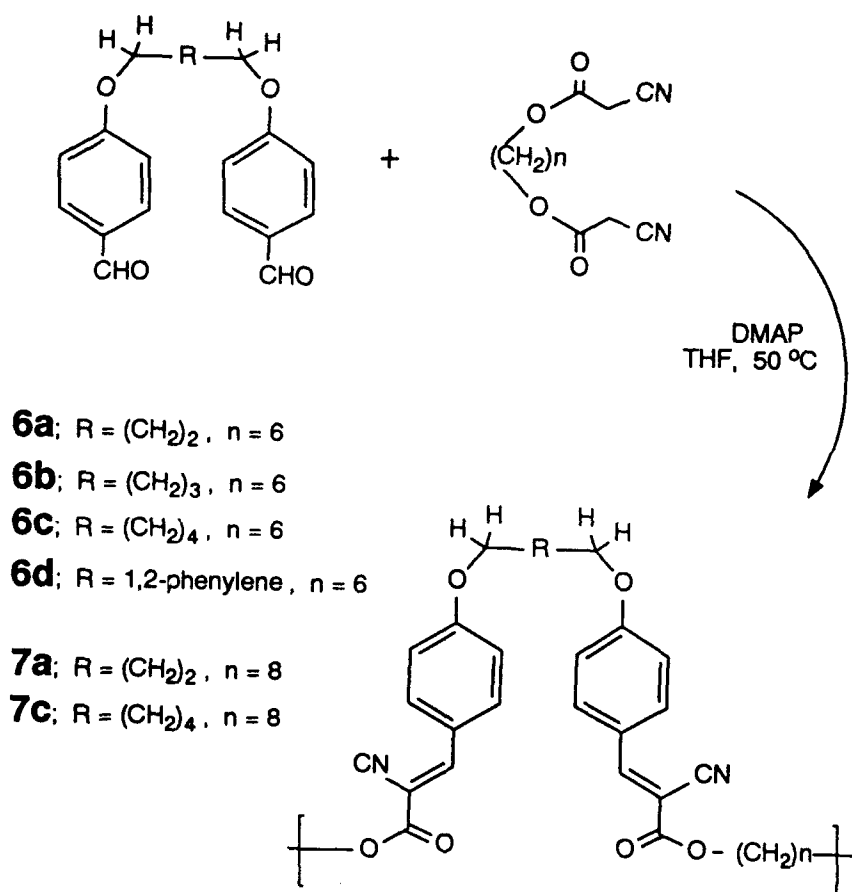
Insert Table 1 here

The polymerization of **3** using DMAP proceeds smoothly at ambient temperature and in a relatively short time frame. The stereochemistry about the alkene is assigned the *E*-geometry based on comparison of the NMR chemical shift of the vinyl proton to related systems.⁵ Other mild bases such as potassium carbonate can be utilized with similar success. The remarkably mild reaction conditions for the Knoevenagel polycondensation technique are the most outstanding feature when contrasting the two polymerization techniques. Mild reaction conditions are harmonious with excellent functional group tolerance and thus eliminated the problem of depolymerization due to excessive temperatures. The excellent solubility of **5** in most organic solvents (~10% by weight) is most likely a consequence of the mild reaction conditions.

The Knoevenagel polycondensation technique has been applied to the copolymerization of monomers **4** with *bis*(cyanoacetate) monomers (Scheme 3). The latter monomers are easily prepared from treatment of the appropriate diol with excess ethyl cyanoacetate and a transesterification catalyst.¹³ The accordion copolymers are prepared in high yield and obtained in analytical pure form after precipitation from hexanes. In the case of **6a** and **6c** the polymeric products are insoluble and precipitate as the polymerization reactions proceed. Utilization of the *bis*(cyanoacetate) obtained from 1,8-octandiol afforded copolymers **7a** and **7c**. These latter polymers are soluble in organic

solvents, but of modest molecular weight (see Table 1). We observe a single gemometric isomer for the copolymers, and as above, is assigned the *E*-isomer.

Scheme 3



Thermal analysis of the polymers is carried out under a nitrogen atmosphere. Differential scanning calorimetry (DSC) analysis of the polymers displays only *T_m*'s with no sign of glass transitions (Figure 1). The scanning rate was 10.0 °C and the results

were obtained from heating scans. After finishing a DSC scan the rapid cooling of the sample would diminish crystallinity in the sample. No apparent glass transitions are observed concomitant with the loss of crystallinity. However, if slow cooling of the sample was carried out (5 °C/min), recrystallization occurred.

Thermal gravimetric analysis (TGA) of the polymers showed good thermal stability to 300+ °C under an atmosphere of nitrogen. The break points for thermal decomposition occurred in the vicinity of 370 °C for for both the linear and accordion type polymers (see Table 1).

Insert Figure 1 here

Concluding Remarks

This work demonstrates that polymers containing NLO-phores are readily available through a Knoevenagel polycondensation technique. The polymerization technique should prove quite versatile because of the very mild reaction conditions and the availability of suitable monomers. We have presented the synthesis of both linear and accordion main-chain NLO polymers using the Knoevenagel polycondensation technique. Future work in our laboratory will focus on extending the scope of this reaction to include more functional elaborate organic and organometallic monomers.

Experimental Section

Methods. All manipulations of compounds and solvents were carried out by using standard Schlenk techniques. Solvents were degassed and purified by distillation under nitrogen from standard drying agents. Spectroscopic measurements utilized the following instrumentation: ^1H NMR, Varian XL 300; ^{13}C NMR, Varian XL 300 (at 75.4 MHz). NMR chemical shifts are reported in δ versus Me_4Si in ^1H NMR and assigning the CDCl_3 resonance at 77.00 ppm in ^{13}C spectra. Infrared, Perkin Elmer 1750 FT-IR; UV-Vis, hp-8452A. The DCC, ethyl cyanoacetate (98% purity), cyanoacetic acid, $\text{Ti}(\text{OC}_4\text{H}_9)_4$, p-hydroxybenzaldehyde, 6-chlorohexanol, 1,4-diiodobutane, 1,5-diiodopentane, 1,6-diiodohexane, 1,8-octanediol, and 1,6-hexanediol were purchased from Aldrich Chemical Co. and used as received. The K_2CO_3 (granular, AR grade, Mallinckrodt) was purchased from Baxter. The *bis*(cyanoacetates), $\text{CNCH}_2\text{CO}_2(\text{CH}_2)_6\text{O}_2\text{CCH}_2\text{CN}$ and $\text{CNCH}_2\text{CO}_2(\text{CH}_2)_8\text{O}_2\text{CCH}_2\text{CN}$, were prepared in similar manner as reported.¹² Thermal analysis of the polymers was performed using a Perkin Elmer TGA7 and DSC7 station. GPC data was collected on a Varian 5000 HPLC employing a PL size-exclusion column (300 x 7.5 mm, 5 μ particle size) using the mixed-pore size. Molecular weight data is referenced relative to polystyrene standards. Elemental analyses were performed at Atlantic Microlab Inc, Norcross, Georgia.

Preparation of {4-[CO₂Et(CN)C=CH]C₆H₄O(CH₂)₆OH} (2). A Schlenk flask was charged with 4-CHOC₆H₄O(CH₂)₆OH (0.5 g, 2.3 mmol), $\text{CNCH}_2\text{CO}_2\text{Et}$ (0.28 g, 2.5 mmol), K_2CO_3 (0.93 g, 6.8 mmol), THF (15 mL), and then heated to reflux for 4 h. The mixture was allowed to cool and then diluted with water. The mixture was extracted with diethyl

ether (2 x 150 mL), the organic layers were then combined, washed with brine, and finally dried over K_2CO_3 . The solvents were removed under reduced pressure and the crude product was crystallized from EtOAc/hexanes (1/2, v/v) to afford pure 2 as a yellow crystalline solid (0.71 g, 84% mp 94-95°C). 1H NMR ($CDCl_3$) δ 8.15 (s, 1 H, \underline{CHO}), 7.97 (d, J = 8.6 Hz, 2 H, Ar), 6.94 (d, J = 8.6 Hz, 2 H, Ar), 4.33 (q, J = 7.3 Hz, 2 H, $\underline{CH_2O_2C}$), 4.01 (t, J = 6.3 Hz, 2 H, $\underline{CH_2OAr}$), 3.65 (t, J = 6.6 Hz, 2 H, $\underline{CH_2OH}$), 1.82-1.34 (m, 8 H, $\underline{CH_2's}$); ^{13}C NMR ($CDCl_3$) δ 163.4 ($\underline{CO_2}$), 154.4 ($\underline{=C(CN)}$), 133.7 (Ar CH), 124.2 ($\underline{=CHAr}$), 116.0 9 (\underline{CN}), 115.2 (Ar CH), 68.3 ($\underline{CH_2OAr}$), 66.0 ($\underline{CH_2O_2C}$), 62.8 ($\underline{CH_2OH}$), 32.6, 29.0, 25.8, 25.5 ($\underline{CH_2's}$), 14.2 ($\underline{CH_3}$); IR (CH_2Cl_2) $\nu_{C=O}$ 1719.0 cm^{-1} . Anal. Calcd for $C_{18}H_{23}O_4N$: C, 68.12; H, 7.30%. Found C, 68.20; H, 7.29%.

Preparation of (4-(CHO) $C_6H_4O(CH_2)_6O_2CCH_2CN$) (3). A Schlenk flask was charged with 4- $CHOC_6H_4O(CH_2)_6OH$ (5.00 g, 22.5 mmol), $CNCH_2CO_2H$ (1.92 g, 22.5 mmol), DCC (4.65 g, 22.5 mmol), CH_2Cl_2 (20 mL), and then allowed to react at 0 °C with stirring for 2 h. The mixture was filtered through a pad (4 x 7 cm) of deactivated silica gel and the pad washed with chloroform/methanol (200 mL, 50/1, v/v). The solvents were removed under reduced pressure and the crude product recrystallized from $CHCl_3$ /hexanes (1/5, v/v) to afford pure 3 as a yellow crystalline solid (6.65 g, 72%, mp 56-57 °C). 1H NMR ($CDCl_3$) δ 9.86 (s, 1 H, \underline{CHO}), 7.81 (d, J = 7.2, 2 H, Ar), 6.97 (d, J = 7.2, 2 H, Ar), 4.21 (t, J = 6.6, 2 H, $\underline{CH_2OAr}$), 4.03 (t, J = 6.4, 2 H, $\underline{CH_2CO_2}$), 3.45 (s, 2 H, $\underline{CH_2CN}$), 1.84-1.44 (m, 8 H, $\underline{CH_2's}$); ^{13}C NMR ($CDCl_3$) δ 190.8 (\underline{CHO}), 164.1 ($\underline{CO_2}$), 162.9 (Ar C), 131.9 (Ar CH), 129.8 (Ar C), 114.7 (Ar CH), 113.0 (\underline{CN}), 68.1 ($\underline{CH_2O}$), 66.8 ($\underline{CH_2CN}$), 28.8, 28.2, 25.5, 24.7 ($\underline{CH_2's}$); IR (CH_2Cl_2) $\nu_{C=O}$ 1751 cm^{-1} . Anal. Calcd for

$C_{16}H_{19}NO_4$: C, 66.43; H, 6.62%. Found: C, 66.30; H, 6.65%.

Preparation of {4-CHOC₆H₄OCH₂CH₂}₂ (4a). A Schlenk flask was charged with *p*-hydroxybenzaldehyde (4.98 g, 40.3 mmol), diiodobutane (5.00 g, 16.0 mmol), K₂CO₃ (5.00 g, 36.2 mmol), DMF (20 mL), and then heated at reflux for 12 h. The mixture was allowed to cool and then diluted with water. The mixture was extracted with chloroform (2 x 150 mL), the organic layers combined, washed with brine, and then dried over K₂CO₃. The solvents were removed under reduced pressure and the crude product was purified by recrystallization from CHCl₃/hexanes (1/5, v/v) to afford pure **4a** as a light-purple crystalline solid suggesting the presence of traces of iodine (4.79 g, 72%, mp 99-100 °C, lit.¹¹ mp 103-104 °C). ¹³C NMR (CDCl₃) δ 190.8 (CHO), 163.9 (Ar C), 132.1 (Ar CH), 130.0 (Ar C), 114.8 (Ar CH), 67.7 (CH₂O), 25.8 (CH₂); IR (CH₂Cl₂) ν_{C=O} 1689 cm⁻¹.

Preparation of {4-CHOC₆H₄OCH₂CH₂}₂CH₂ (4b). A Schlenk flask was charged with *p*-hydroxybenzaldehyde (2.83 g, 23.2 mmol), diiodopentane (3.00 g, 9.3 mmol), K₂CO₃ (3.00 g, 21.7 mmol), DMF (15 mL), and then heated at reflux for 12 h. The mixture was allowed to cool and then diluted with water. The mixture was extracted with chloroform (2 x 150 mL), the organic layers were then combined, washed with brine, and finally dried over K₂CO₃. The solvents were removed under reduced pressure and the crude product was purified by recrystallization from CHCl₃/hexanes (1/5, v/v) to afford pure **4b** as a light-pink crystalline solid suggesting the presence of traces of iodine (1.67 g, 58%, mp 81-82 °C). ¹H NMR (CDCl₃) δ 9.88 (s, 2 H, CHO), 7.83 (d, *J* = 8.8 Hz, 4 H, Ar), 6.99 (d, *J* = 8.8 Hz, 4 H, Ar), 4.06 (t, *J* = 6.4 Hz, 4 H, CH₂O), 1.57-1.87 (m, 6 H,

CH₂'s); ¹³C NMR (CDCl₃) δ 190.8 (CHO), 163.5 (Ar C), 132.0 (Ar CH), 129.9 (Ar C), 114.7 (Ar CH), 68.1 (CH₂O), 28.8, 22.7 (CH₂'s); IR (CH₂Cl₂) ν_{C=O} 1688 cm⁻¹. Anal. Calcd for C₁₉H₂₀O₄: C, 73.06; H, 6.45%. Found: C, 72.89; H, 6.46%.

Preparation of [4-CHOC₆H₄OCH₂CH₂CH₂]₂ (4c). A Schlenk flask was charged with *p*-hydroxybenzaldehyde (2.71 g, 22.2 mmol), diiodohexane (3.00 g, 8.9 mmol), K₂CO₃ (3.00 g, 21.7 mmol), DMF (15 mL), and then heated at reflux for 12 h. The mixture was allowed to cool and then diluted with water (100 mL). The mixture was extracted with chloroform (2 x 150 mL) and the organic layers were combined, washed with brine (50 mL), and then dried over K₂CO₃. The solvents were removed under reduced pressure and the crude product crystallized from CHCl₃/ hexanes (1/5, v/v) to afford pure 4c as an off-white crystalline solid (1.94 g, 67%, mp 105-106 °C, lit.¹¹ mp 106-10 °C). ¹H NMR (CDCl₃) δ 9.89 (s, 2 H, CHO), 7.83 (d, *J* = 8.6 Hz, 4 H, Ar), 6.99 (d, *J* = 8.6 Hz, 4 H, Ar) 4.09 (t, *J* = 6.3 Hz, 4 H, CH₂O), 1.91 (m, 4 H, CH₂'s), 1.68 (m, 4 H, CH₂'s); ¹³C NMR (CDCl₃) δ 190.8 (CHO), 164.0 (Ar C), 132.0 (Ar CH), 130.0 (Ar C) 114.7 (Ar CH), 68.2 (CH₂O), 28.9, 25.8 (CH₂'s); IR (CH₂Cl₂) ν_{C=O} 1688 cm⁻¹.

Preparation of [1,2-(4-CHOC₆H₄OCH₂)₂C₆H₄] (4d). A Schlenk flask was charged with *p*-hydroxybenzaldehyde (15.40 g, 125.8 mmol), 1,2-bis(chloromethyl)benzene (10.0 g, 57.2 mmol), K₂CO₃ (15.00 g, 108.5 mmol), DMF (30 mL), and then heated at reflux for 24 h. The mixture was allowed to cool, diluted with water, and then extracted with chloroform (2 x 150 mL). The organic layers were combined, washed with water (2 x 100

mL), brine (100 mL), and then dried over K_2CO_3 . The solvents were removed under reduced pressure and the crude product was purified by passing it through a column of alumina (4 x 30 cm) and eluting with a mixture of EtOAc/Hexanes (300 mL, 80/20, v/v). Evaporation of the solvents under reduced pressure afforded pure **4d** as a white microcrystalline solid (15.7 g, 80%, mp 140-141 °C). 1H NMR ($CDCl_3$) δ 9.87 (s, 2 H, CHO), 7.82 (d, J = 4.8 Hz, 4 H, Ar), 7.40-7.50 (m, 4 H, Ar), 7.03 (d, J = 4.8 Hz, 4 H, Ar), 5.25 (s, 4 H, CH_2O); ^{13}C NMR ($CDCl_3$) δ 190.6 (CHO), 163.5 (Ar C), 134.3 (Ar C), 132.0 (Ar CH), 130.0 (Ar C), 129.3, 129.0 (Ar CH's), 115.0 (Ar C), 68.3 (CH_2O); IR (CH_2Cl_2) $\nu_{C=O}$ 1695 cm^{-1} Anal. Calcd for $C_{22}H_{18}O_4$: C, 76.29; H, 5.24%. Found: C, 75.65; H, 5.27%.

Preparation of $[=CHC_6H_4O(CH_2)_6O_2C(CN)C=]_n$ (5). A Schlenk flask was charged with **3** (0.50 g, 1.7 mmol), DMAP (0.42 g, 3.5 mmol), THF (10mL) and the contents allowed to react with stirring at ambient temperature for 4 h. The solvents were evaporated under reduced pressure and the crude product was recrystallized from $CHCl_3$ /pentane (1/5, v/v) to afford **5** as a yellow solid (0.47 g, 77%). 1H NMR ($CDCl_3$) δ 8.15 (s, 1 H, $=\underline{CH}$), 7.98 (d, J = 9.0, 2 H, Ar), 6.98 (d, J = 9.0, 2 H, Ar), 4.32 (t, J = 6.5, 2 H, $\underline{CH_2OAr}$), 4.06 (t, J = 6.4, 2 H, $\underline{CH_2O_2C}$), 1.86-1.53 (m, 8 H, CH_2 's); ^{13}C NMR ($CDCl_3$) δ 163.4 (CO_2), 154.4 (Ar C), 134.4 (Ar CH), 124.2 ($=\underline{C(CN)CO_2}$), 117.0 ($=\underline{CHAr}$), 115.9 (Ar CH), 114 (\underline{CN}), 68.2 ($\underline{CH_2O}$), 66.2 ($\underline{CH_2O_2C}$), 28.9, 28.4, 26.2 (CH_2 's). Anal. Calcd for $C_{16}H_{17}O_3N$: C, 70.83; H, 6.32%. Found: C, 70.68; H, 6.34%.

Preparation of $[=CHC_6H_4O(CH_2)_5OC_6H_4[CH=C(CN)CO_2(CH_2)_6O_2C(CN)C=]]_n$ (6b)
 A Schlenk tube was charged with **4b** (0.2 g, 0.6 mmol), $CNCH_2CO_2(CH_2)_6O_2CCH_2CN$

(0.16 g, 0.6 mmol), DMAP (0.24 g, 1.92 mmol), THF (10 mL) and the contents allowed to react at room temp. with stirring for 4 h. The reaction was stopped and the solvent was evaporated under reduced pressure and the crude product was purified by recrystallization from CHCl_3 /pentane (1/5, v/v) to afford pure **6b** as a yellow solid (0.28 g, 85%). ^1H NMR (CDCl_3) δ 8.16 (s, 2 H, $=\text{CH}$), 7.98 (d, J = 8.6 Hz, 2 H, Ar), 6.97 (d, J = 8.6 Hz, 2 H, Ar), 4.32 (t, J = 6.2 Hz, 4 H, CH_2OAr), 4.08 (t, J = 7.8 Hz, 4 H, $\text{CH}_2\text{O}_2\text{C}$), 1.93-1.49 (m, 14 H, CH_2 's); ^{13}C NMR (CDCl_3) δ 163.2 (Ar C), 161.9 (CO_2), 154.4 ($=\text{C}(\text{CN})\text{CO}_2$), 133.7 (Ar CH), 124.4 ($=\text{CHAr}$), 115.2 (Ar CH), 68.1 ($\text{CH}_2\text{O}_2\text{C}$), 66.3 (CH_2OAr), 28.8, 28.4, 25.5, (CH_2 's). Anal. Calcd for $[\text{C}_{31}\text{H}_{32}\text{N}_2\text{O}_6]_{53}$: C, 70.40; H, 6.06%. Found: C, 69.77; H, 6.20%.

*Preparation of [1-{ $\text{CHC}_6\text{H}_4\text{OCH}_2$ }-2-{ $\text{CH}=\text{C}(\text{CN})\text{CO}_2(\text{CH}_2)_6\text{O}_2\text{C}(\text{CN})\text{C}=\text{}$ }- $\text{C}_6\text{H}_4\text{OCH}_2$] C_6H_4] $_n$ (**6d**). A Schlenk tube was charged with **4d** (0.20 g, 0.6 mmol), $\text{CNCH}_2\text{CO}_2(\text{CH}_2)_6\text{O}_2\text{CCH}_2\text{CN}$ (0.15 g, 0.6 mmol), DMAP (0.21 g, 0.70 mmol), THF (10 mL) and the contents allowed to react at 50 °C with stirring for 4 h. The reaction was stopped and the solvent was evaporated under reduced pressure. The crude product was recrystallized from CHCl_3 /pentane (1/5, v/v) to afford pure **6d** as a light yellow solid (0.26 g, 81%). ^1H NMR (CDCl_3) δ 8.17 (s, 2 H, $=\text{CH}$), 8.0 (d, J = 8.4 Hz, 2 H, Ar), 7.52 (m, 2 H, Ar), 7.44 (m, 2 H, Ar), 5.27 (s, 4 H, CH_2OAr), 4.32 (t, J = 6.0 Hz, 4 H, $\text{CH}_2\text{O}_2\text{C}$), 1.81-1.52 (m, 8 H, CH_2 's); ^{13}C NMR (CDCl_3) δ 163.0 (Ar C), 162.5 (CO_2), 154.2 ($=\text{CCNCO}_2$), 134.2 (Ar C), 133.7 (Ar CH), 129.4 (Ar C), 129.0 (Ar CH), 124.8 ($=\text{CHPh}$), 115.4 (Ar CH), 68.4 (CH_2OAr), 66.2 ($\text{CH}_2\text{O}_2\text{C}$), 28.4, 25.5 (CH_2 's). Anal. Calcd for $[\text{C}_{34}\text{H}_{30}\text{N}_2\text{O}_6]_{25}$: C, 72.34; H, 5.33%. Found: C, 71.95; H, 5.60%.*

Preparation of $[=\text{CHC}_6\text{H}_4\text{O}(\text{CH}_2)_6\text{OC}_6\text{H}_4\text{CH}=\text{C}(\text{CN})\text{CO}_2(\text{CH}_2)_8\text{O}_2\text{C}(\text{CN})\text{C}=\text{}]_n$ (7c) A Schlenk tube was charged with **4c** (0.20 g, 0.60 mmol), $\text{CNCH}_2\text{CO}_2(\text{CH}_2)_8\text{O}_2\text{CCH}_2\text{CN}$ (0.17 g, 0.6 mmol), DMAP (0.15 g, 1.2 mmol), THF (10 mL), and the contents allowed to react at ambient temperature for 8 h. The reaction was stopped and the solvent was evaporated under reduced pressure. The crude product was purified by recrystallization from CHCl_3 /pentane (1/2, v/v) to afford **6c** as a white solid (0.27 g, 77%). ^1H NMR (CDCl_3) δ 8.16 (s, 2 H, $=\text{CH}$), 8.01 (d, $J = 9.0$ Hz, 2 H, Ar), 6.97 (d, $J = 9.0$ Hz, 2 H, Ar), 4.30 (t, $J = 6.5$ Hz, 4 H, CH_2OAr), 4.06 (t, $J = 6.4$ Hz, 4 H, $\text{CH}_2\text{O}_2\text{C}$), 1.86-1.40 (m, 20 H, CH_2 's); ^{13}C NMR (CDCl_3), δ 163.2 (Ar C), 163.0 (CO_2), 154.2 ($=\text{CCNCO}_2$), 133.7 (Ar CH), 124.2 ($=\text{CHAr}$), 116.1 (CN), 115.2 (Ar CH), 68.1 (CH_2OPh), 66.3 ($\text{CH}_2\text{O}_2\text{C}$), 29.03, 28.9, 28.5, 25.8, 25.7 (CH_2 's). Anal. Calcd for $[\text{C}_{34}\text{H}_{38}\text{N}_2\text{O}_6]_{12}$: C, 71.09; H, 6.63%. Found: C, 70.92; H, 6.78%.

$[=\text{CHC}_6\text{H}_4\text{O}(\text{CH}_2)_4\text{OC}_6\text{H}_4\text{CH}=\text{C}(\text{CN})\text{CO}_2(\text{CH}_2)_8\text{O}_2\text{C}(\text{CN})\text{C}=\text{}]_n$ (7d) Polymer **7d** was prepared in 54% isolated yield using a procedure outlined for polymer **6b**. Spectroscopic and analytical data: ^1H NMR (CDCl_3) δ 8.19 (s, 2 H, $=\text{CH}$), 8.02 (d, $J = 9.0$ Hz, 4 H, Ar), 6.99 (d, $J = 9.0$ Hz, 4 H, Ar), 4.32 (t, $J = 6.7$ Hz, 4 H, CH_2OAr), 4.16 (br s, 4 H, CH_2CO_2), 2.06-1.39 (m, 16 H, CH_2 's); ^{13}C NMR (CDCl_3), δ 163.2 (Ar C), 163.1 (CO_2), 154.1 ($=\text{C}(\text{CN})$), 133.7 (Ar CH), 124.1 ($=\text{CHAr}$), 116.0 (CN), 115.2 (Ar CH), 68.1 (CH_2OAr), 66.3 ($\text{CH}_2\text{O}_2\text{C}$), 29.0, 28.9, 28.5, 25.8, 25.7 (CH_2 's).

Acknowledgment. Support for this research was furnished by the Office of Naval Research and is gratefully acknowledged.

References & Notes

1. For a general treatment of NLO materials see: "Nonlinear Optical and Electroactive Polymers," Eds.; Prasad, P. N., Ulrich, D. R., Plenum Press, New York 1988. "Organic Materials for Non-linear Optics" (Spec. Publ. No. 69), The Royal Society of Chemistry, London 1989. "Organic Materials for Non-linear Optics II" (Spec. Publ. No. 91), The Royal Society of Chemistry, London 1991. "Materials for Nonlinear Optics," Marder, S. R., Sohn, J. E., Stucky, G. D., Eds.; ACS Symp. Series 455, American Chemical Society, Washington DC 1991 and references cited therein.
2. Stamatoff, J.; DeMartino, R.; Hass, D.; Khanarian, G.; Man, H. T.; Norwood, R.; Yoon, H. N. *Die Angew. Makromol. Chemie* **1990**, *183*, 151 and references cited therein.
3. For recent examples see: Hayden, L. M.; Sauter, G. F.; Ore, F. R.; Pasillas, P. L.; Hoover, J. M.; Lindsay, G. A.; Henry, R. A. *J. Appl. Phys.* **1990**, *68*, 456. Zhende, N.; Leslie, T. M.; Padias, A. B., Hall, H. K. jr. *Macromolecules* **1991**, *24*, 2100. Zhao, M.; Bautista, M.; Ford, W. T. *Macromolecules* **1991**, *24*, 844. Allcock, H. R.; Dembek, A. A.; Kim, C.; Devine, R. L. S.; Shi, Y.; Steier, W. H.; Spangler, C. W. *Macromolecules* **1991**, *24*, 1000.
4. Robello, D. R.; Willand, C. S.; Scozzafava, M.; Ulman, A.; Williams, D. J. in "Materials for Nonlinear Optics", Marder, S. R., Sohn, J. E., Stucky, G. D., Eds.; ACS Symp. Series 455, American Chemical Society, Washington DC 1991, pp 279-293.
5. (a) Fuso, F.; Padias, A. B.; Hall, H. K. Jr. *Macromolecules* **1991**, *24*, 1710. (b) Ni, Z.;

- Lesile, T. M.; Padias, A. B.; Hall, H. K. Jr. *Macromolecules* 1991, 24, 2100. (c)
- Green, G. D.; Hall, H. K., Jr.; Mulvaney, J. E.; Noonan, J.; Williams, D. J. *Macromolecules* 1987, 20, 716. (d) Green, G. D.; Weinschenk, J. I.; Mulvaney, J. E.; Hall, H. K., Jr. *Macromolecules* 1987, 20, 722. (e) Hall, H. K., Jr.; Padias, A. B.; Fuso, F.; Ni, Z.; Mitchell, M. A.; Lesile, T. M. In *Multifunctional Materials*, Buckley, A., Gallagher-Daggitt, G., Karasz, F. E., Ulrich, D. R., Eds.; *Mater. Res. Symp. Proc.* 1990, 175, 51.
6. (a) Stenger-Smith, J. D.; Fischer, J. W.; Henry, R. A.; Hoover, J. M.; Lindsay, G. A.; Hayden, L. M. *Makromol. Chem. Rapid Commun.* 1990, 11, 141. (b) Lindsay, G. A.; Fischer, J. W.; Henry, R. A.; Hoover, J. M.; Kubin, R. F.; Seltzer, M. D.; Stenger-Smith, J. D. *Polym. Preprints* 1991, 32(2), 91. Lindsay, G. A.; Stenger-Smith, J. D.; Henry, R. A.; Hoover, J. M.; Kubin, R. F. *SPIE-The International Society for Optical Engineering* 1991, 1497, 418-422. Lindsay, G. A.; Nee, S. F.; Hoover, J. M.; Stenger-Smith, J. D.; Henry, R. A.; Kubin, R. F.; Seltzer, M. D. *Ibid* 1991, 1560, 443.
 7. Wright, M. E.; Toplikar, E. G. *Macromolecules*, this issue. Wright, M. E.; Sigman, M. S. *Macromolecules*, this issue.
 8. March, J. *Advanced Organic Chemistry*, John Wiley & Sons, New York, 3rd edition (1985) pp 670-671 and references cited therein.
 9. Hall and coworkers in ref 5(d) used piperidine and acetic acid in refluxing benzene.
 10. "Reagents for Organic Synthesis," Fieser, L. F.; Fieser, M. Eds., Wiley, New York, 1967, Vol. 1, p. 216.
 11. Donahoe, H. B.; Benjamin, L. E.; Fennoy, L.V.; Greiff, D. J. *Org.Chem.* 1961, 26, 474.

Guilani, B.; Rasco, M. L.; Hermann, C. F. K.; Gibson, H. W. *J. Hetrocyclic Chem.* **1990**, 27, 1007.

12. Chen, M.; Yu, L.; Dalton, L. R.; Shi, Y.; Steier, W. H. *Macromolecules* **1991**, 24, 5421.
13. Leonard, D. P.; Truesdale, J. H.; Scherrer, J. H. *Chem. Abst.* **1990** 112:P160665e.
Heckles, J. S. *Chem. Abst.* **1981**, 94:4577g. For full details on the synthesis and characterization see: Wright, M. E.; Sigman, M. S. *Macromolecules*, this issue.

Table 1. Selected physical and spectroscopic data for polymers 4, 6b, 6d, 7a, and 7c.

Polymer	M_n	M_w	UV-Vis (CH_2Cl_2)	T_m ($^\circ\text{C}$)	TGA (N_2 , break point $^\circ\text{C}$)
$[-\text{CHC}_6\text{H}_4\text{O}(\text{CH}_2)_6\text{O}_2\text{C}(\text{CN})\text{C}=\text{I}_\text{N}$ (transesterification)	6800	14,100	$\lambda_{\text{max}} = 346 \text{ nm}$ ($\epsilon = 3.1 \times 10^4$)	93, 104 ^b	383 ^a
$[-\text{CHC}_6\text{H}_4\text{O}(\text{CH}_2)_6\text{O}_2\text{C}(\text{CN})\text{C}=\text{I}_\text{N}$ (Knoevenagel)	30,100	57,700	$\lambda_{\text{max}} = 346 \text{ nm}$ ($\epsilon = 2.91 \times 10^4$)	123	376
Polymer 6b	26,200	47,600	$\lambda_{\text{max}} = 346 \text{ nm}$ ($\epsilon = 5.44 \times 10^4$)	148	359
Polymer 6d	21,600	35,500	$\lambda_{\text{max}} = 340 \text{ nm}$ ($\epsilon = 5.48 \times 10^4$)	73	
Polymer 7a	3100	6100	$\lambda_{\text{max}} = 346 \text{ nm}$ ($\epsilon = 5.38 \times 10^3$)	192, 205 ^b	
Polymer 7c	9800	16,600	$\lambda_{\text{max}} = 346 \text{ nm}$ ($\epsilon = 2.48 \times 10^4$)	159, 182 ^b , 188 ^b	

^a under a nitrogen atmosphere, ramp rate of 10 $^\circ\text{C}/\text{min}$. Break point is the temperature where a continuous and rapid weight loss began to occur.

^b a minor endotherm possibly due to Liquid crystal behavior.

Captions for Figures

Figure 1. Differential scanning calorimeter plot for polymer **6b**. The analysis was carried out under an atmosphere of nitrogen and at a ramp rate of 10°C/min. This is the initial DSC scan of the material.

Figure 1

